# Electronic Transport Phenomena in Composite Nanocrystalline/Amorphous and Free-Standing Nanocrystalline Thin Films

James Kakalios

School of Physics and Astronomy

The University of Minnesota

# Acknowledgements

- All of this research performed in collaboration with Prof. Uwe R. Kortshagen,

  C. Blackwell, Y. Adjallah, C. Anderson, L. R. Wienkes, David Rowe, K. Bodurtha, J. Trask, Z. Razielli

  and Brendon Jones, Jake Novotsky and Jingyang Sheng

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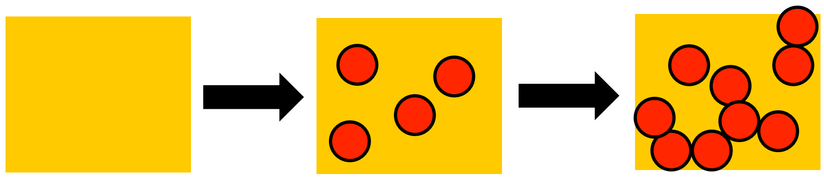
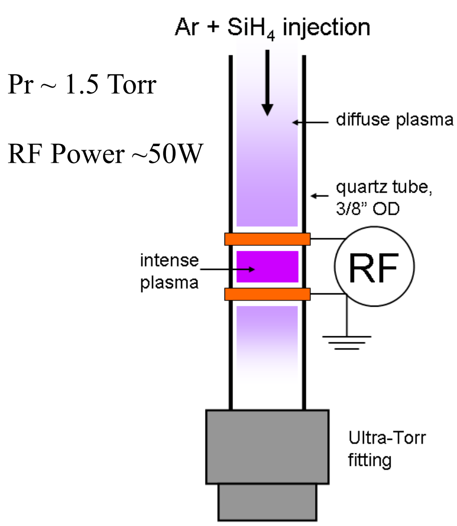
# Composite Amorphous/ Nanocrystalline Thin Films

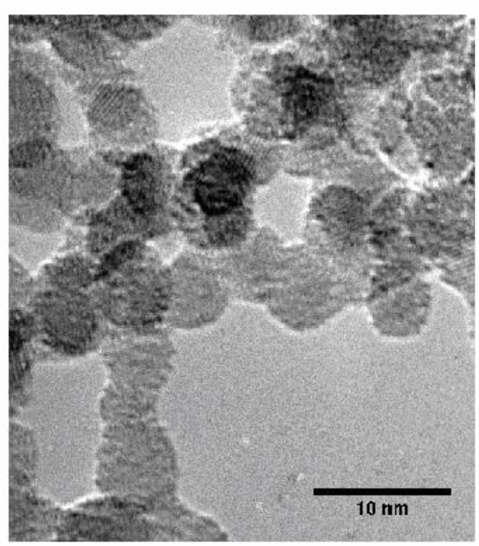
- Thin Film Amorphous Matrix in which Nanocrystallites are Embedded ($X_c \sim 0 - 100\%$)
- Composites Can Combine the Large Area, Thin Film Advantages of Amorphous Silicon with Superior Electronic Properties of Crystalline Silicon
- How Do Transport Properties Change with nc?





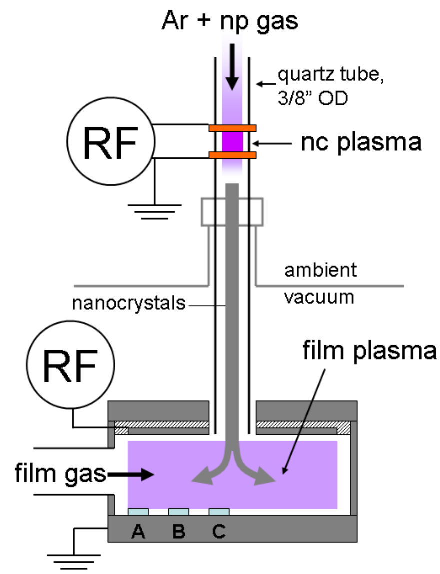
# PECVD Synthesis of Nanocrystals



# Dual Chamber Co-Deposition System

- Nanocrystals are produced in one capacitively coupled PECVD chamber
- In the second chamber a-Si:H film is produced
- The nanoparticles are entrained by a carrier gas and injected in the second chamber where mixed phase film is deposited
- Growth parameters can be separately optimized for both the particles and the amorphous film

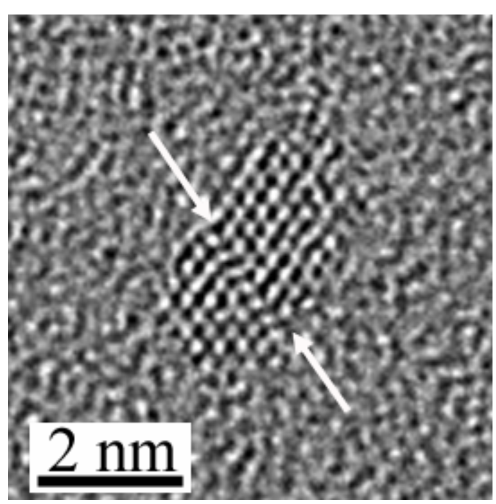



# High Resolution TEM

Si particle ~ 1.5 nm x 3 nm

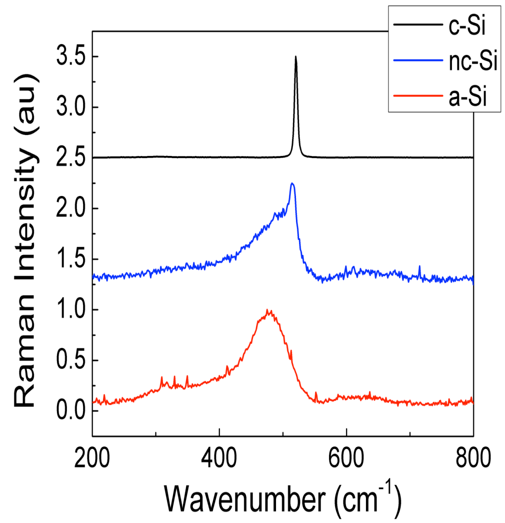
Images taken by Prof. C. B. Carter with a Philips CM 200 FEG with a spherical aberration corrector

with Dr. Markus Lentzen and Prof. Knut Urban (Research Center Jülich, Germany).

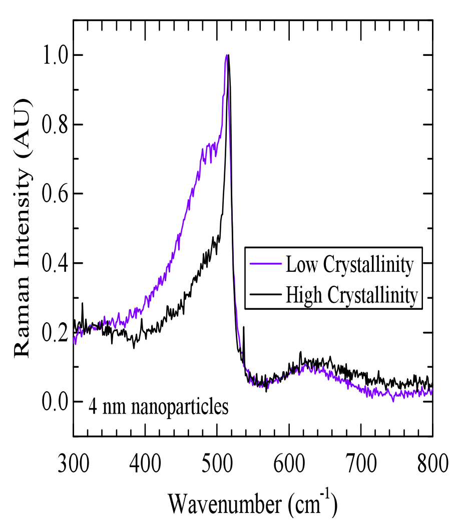



HRTEM image of the
1450 mTorr a/nc-Si:H sample

# Raman Spectrum for c-Si, nc-Si and a-Si

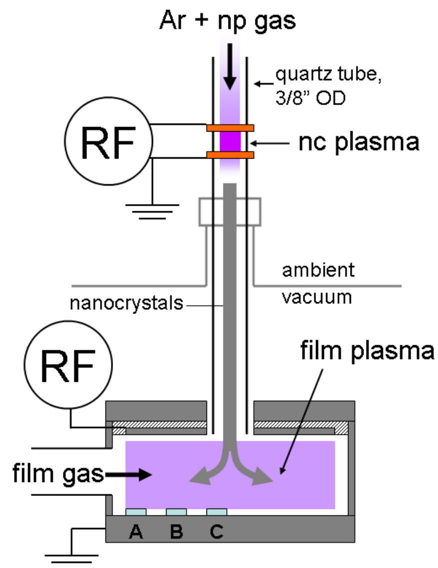


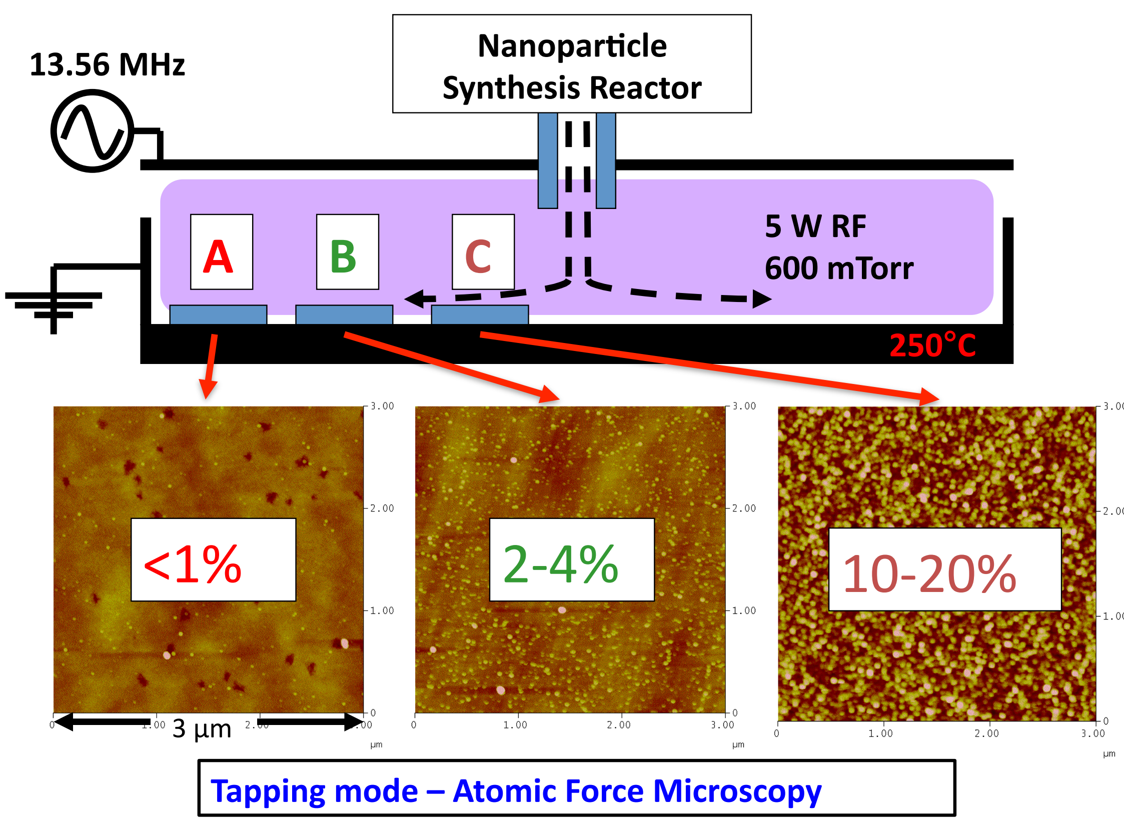

# Raman for nc-Si with varying degree of crystallinity



# Nanocrystal Concentration is Not Uniform

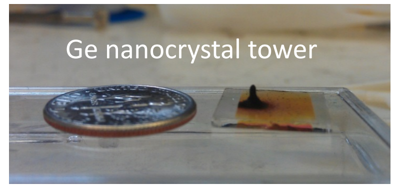
- Concentration of nc in a-Si:H film controlled through gas convection in second chamber




Y. Adjallah, C. Anderson, U. Kortshagen and JK, Journal of Applied Physics **107**, 43704 (2010)

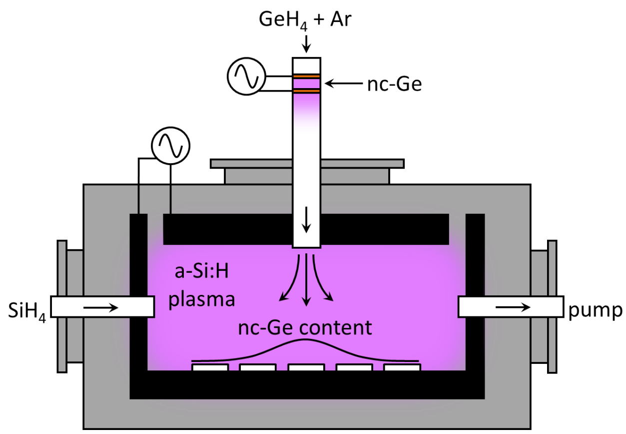
# Germanium nc in a-Si:H



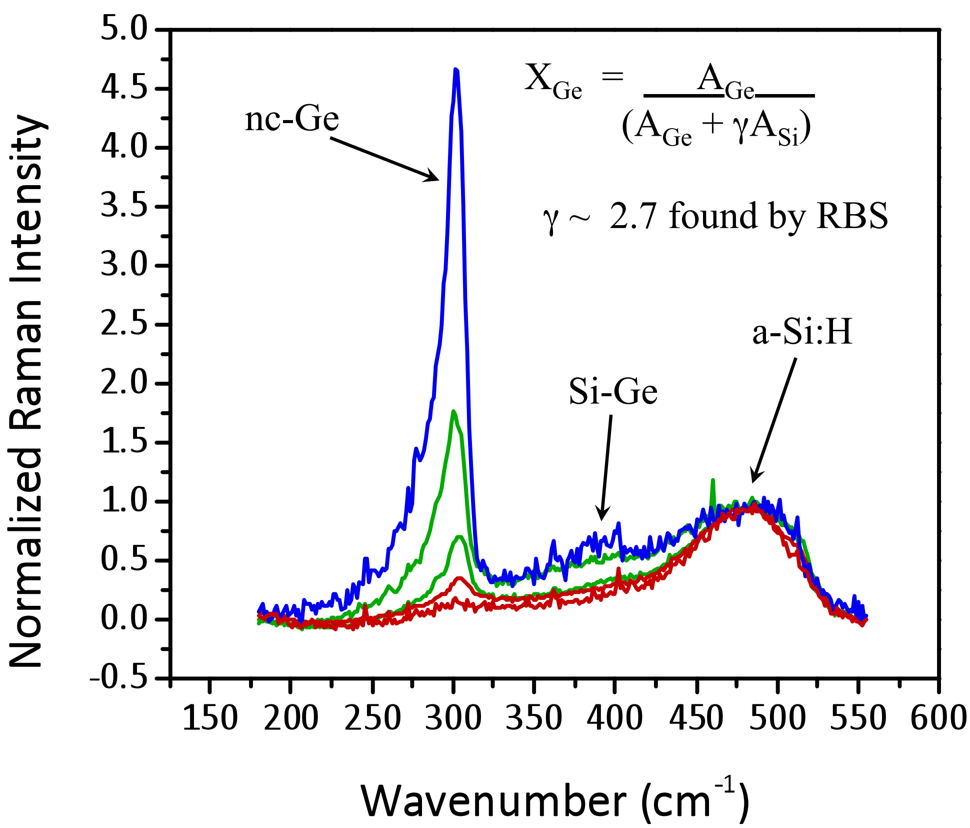

~4nm Ge crystals embedded in a-Si:H matrix

Vary only nc-Ge content across a series of films

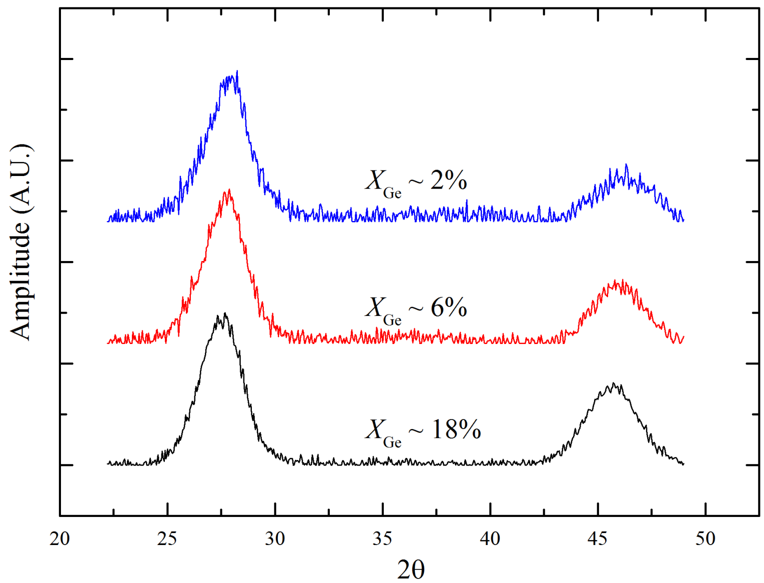
Over multiple runs, nc-Ge content varies from 0 to 75%

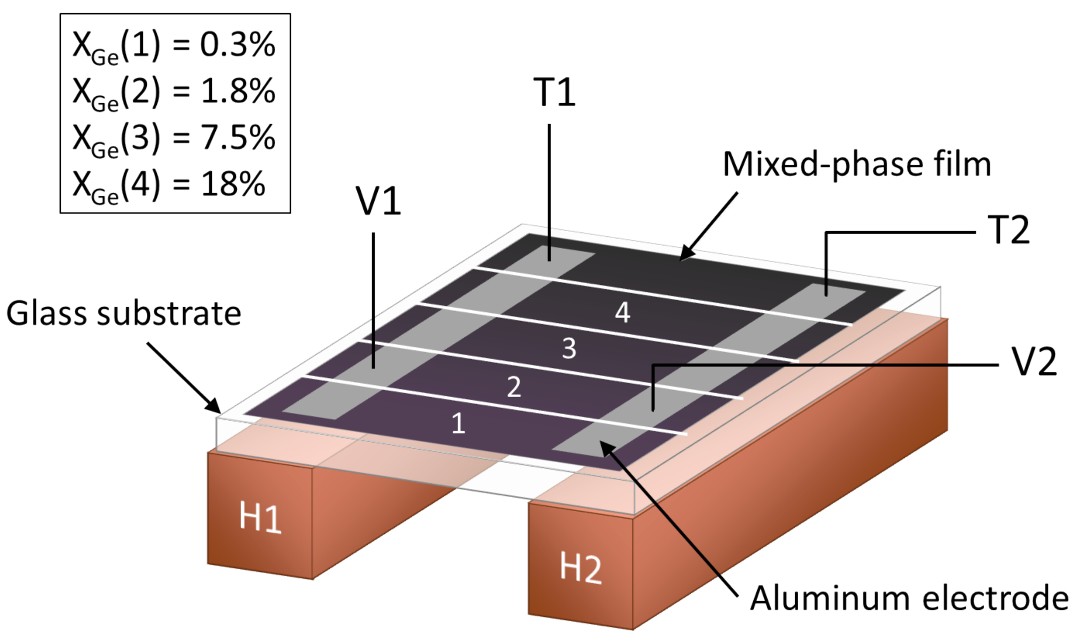


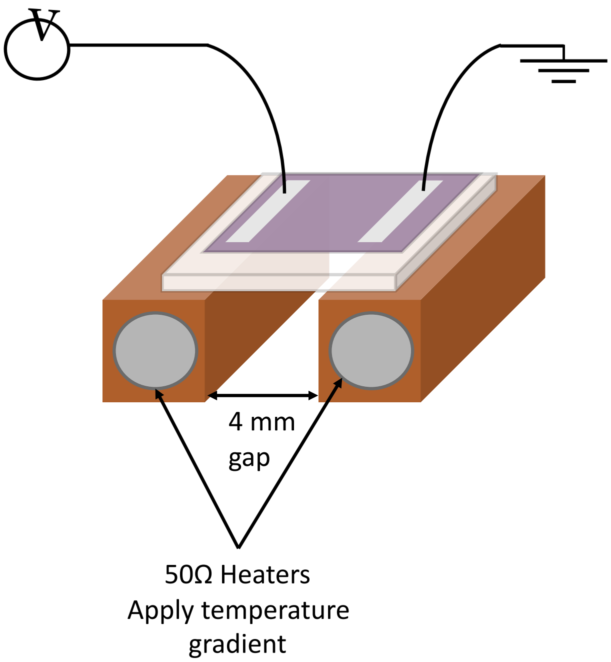


# X-Ray Diffraction Indicates nc diameter ~ 3.5 – 4.5 nm

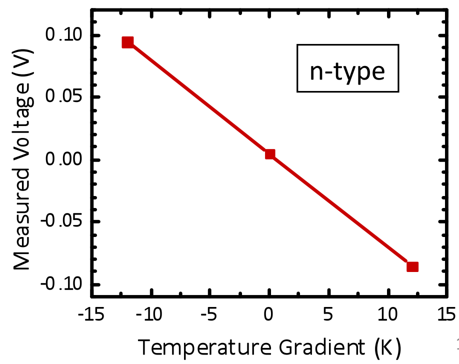


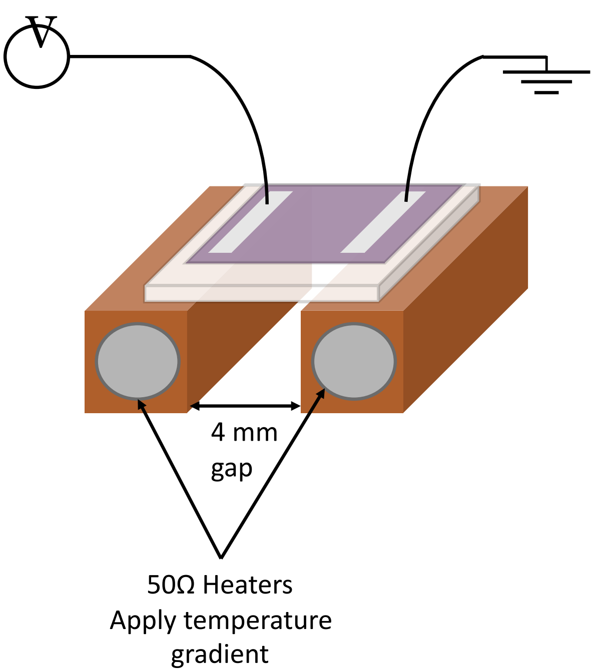



Seebeck coefficient $S = -\frac{V_1 - V_2}{T_1 - T_2}$

| Step | $\boldsymbol{T}_1$ | $\boldsymbol{T}_2$ |
|---|---|---|
| 1) | $T_0 + 6$ | $T_0 - 6$ |
| 2) | $T_0$ | $T_0$ |
| 3) | $T_0 - 6$ | $T_0 + 6$ |

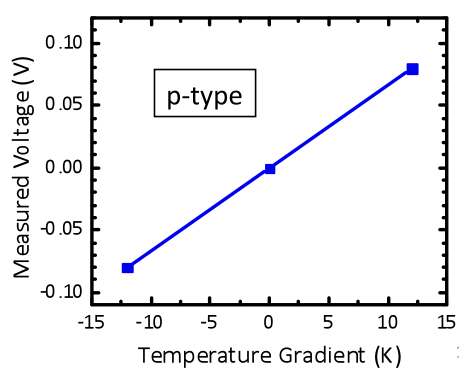



15

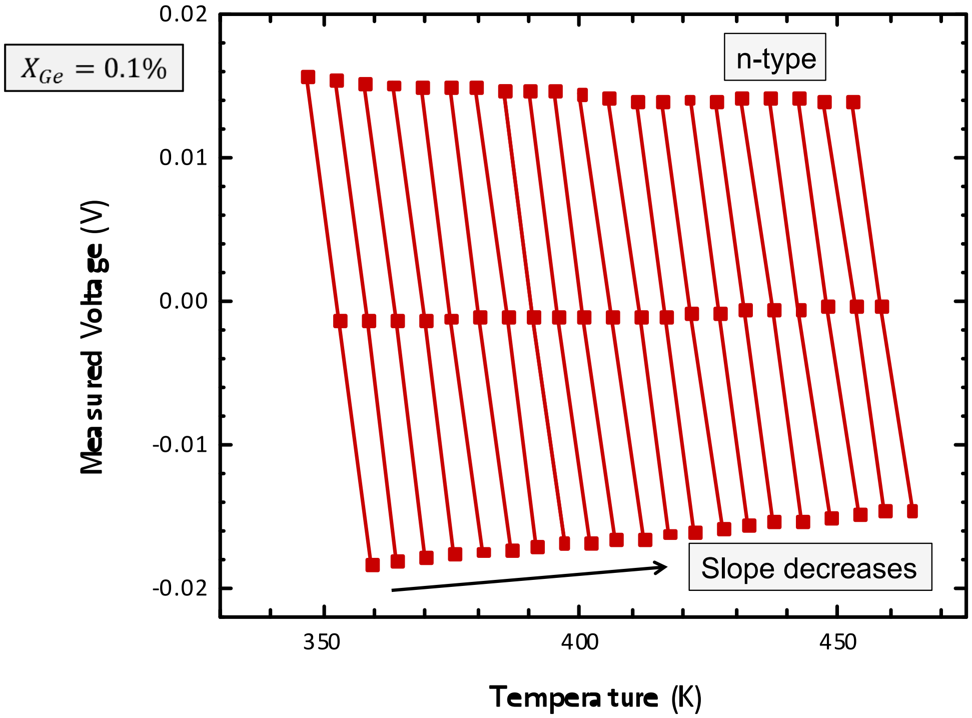



Seebeck coefficient $S = -\frac{V_1 - V_2}{T_1 - T_2}$

| Step | $\boldsymbol{T}_1$ | $\boldsymbol{T}_2$ |
|---|---|---|
| 1) | $T_0 + 6$ | $T_0 - 6$ |
| 2) | $T_0$ | $T_0$ |
| 3) | $T_0 - 6$ | $T_0 + 6$ |

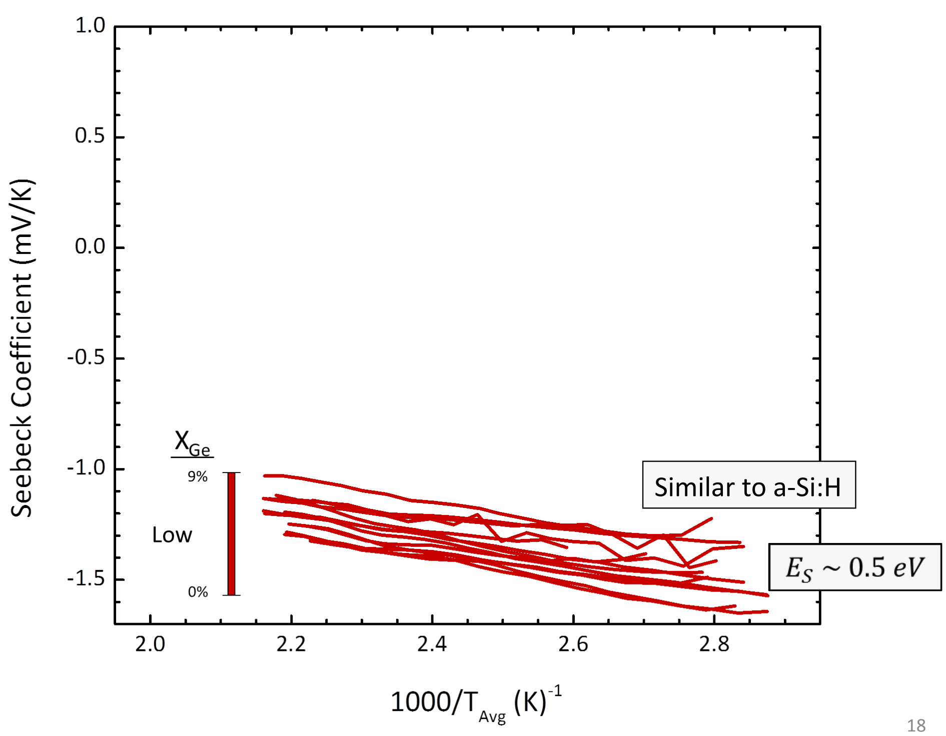



16

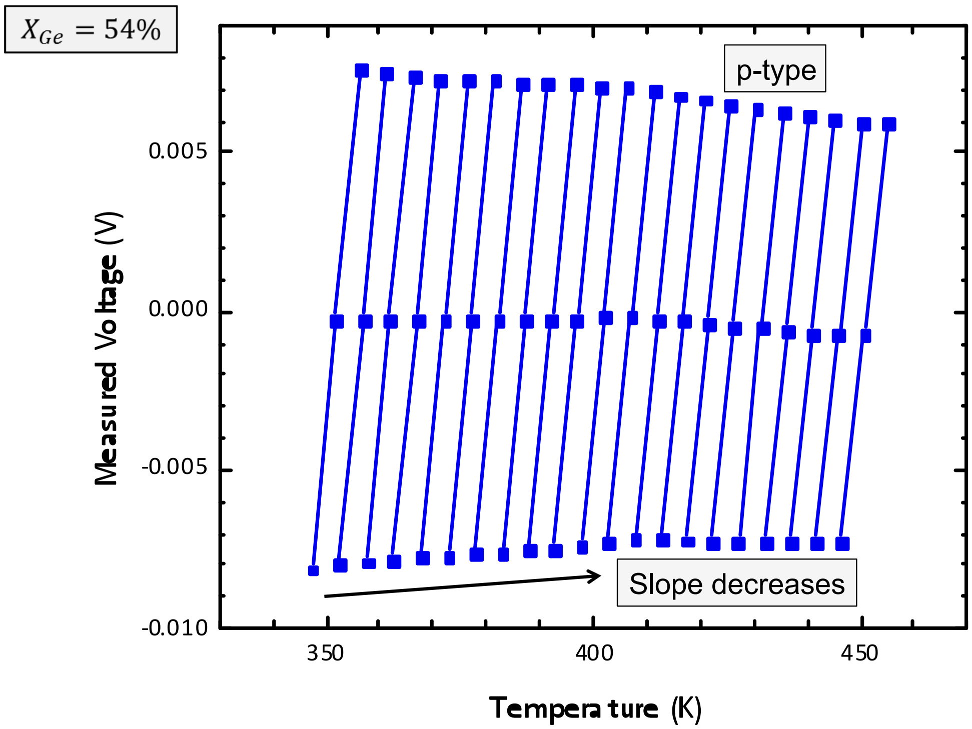


$X_{Ge} = 0.1\%$
n-type
Slope decreases
Measured Voltage (V)
Temperature (K)
0.02
0.01
0.00
-0.01
-0.02
350
400
450



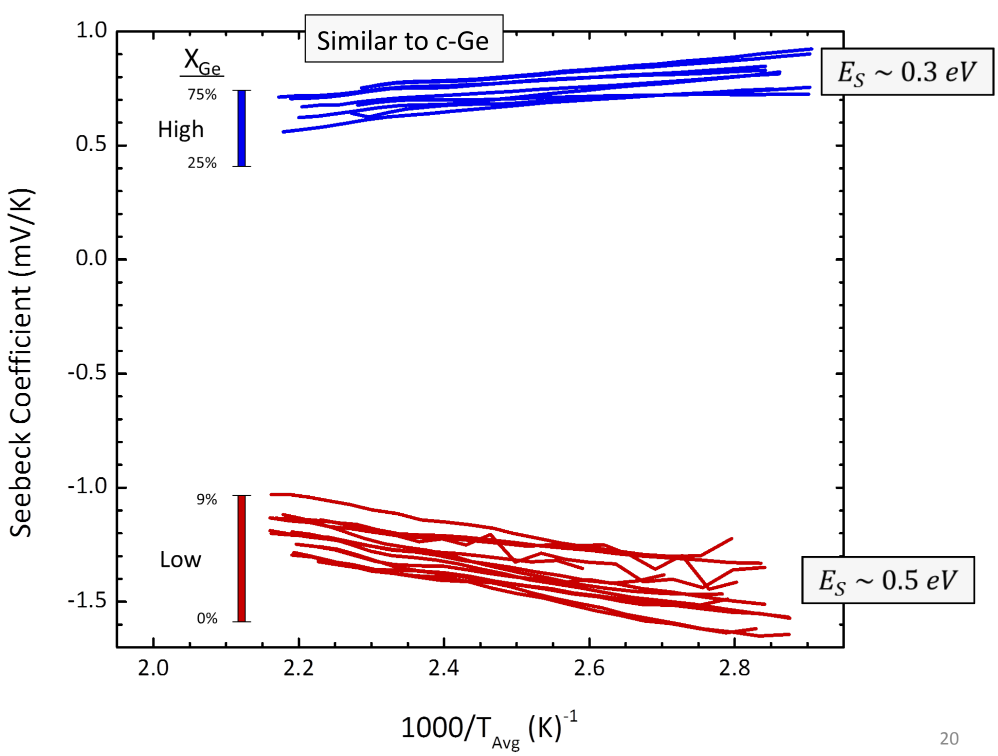



Similar to a-Si:H
$E_S \sim 0.5\ eV$
$X_{Ge}$
9%
Low
0%
Seebeck Coefficient (mV/K)
$1000/T_{Avg}\ (K)^{-1}$
1.0
0.5
0.0
-0.5
-1.0
-1.5
2.0
2.2
2.4
2.6
2.8



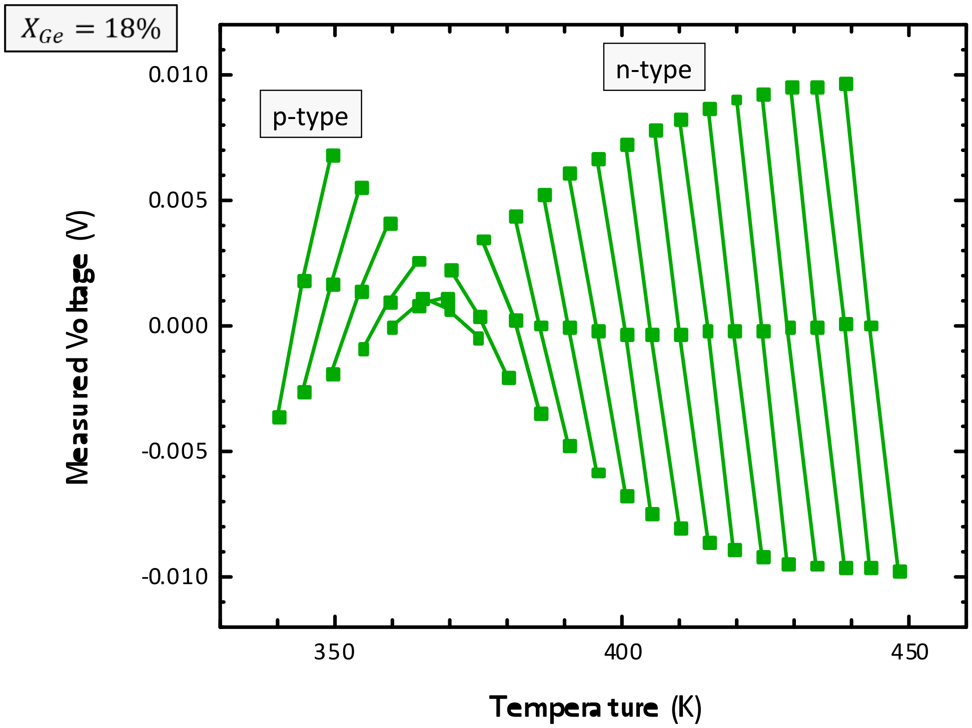
$X_{Ge} = 54\%$
p-type
Slope decreases
Measured Voltage (V)
0.005
0.000
-0.005
-0.010
350
400
450
Temperature (K)


19



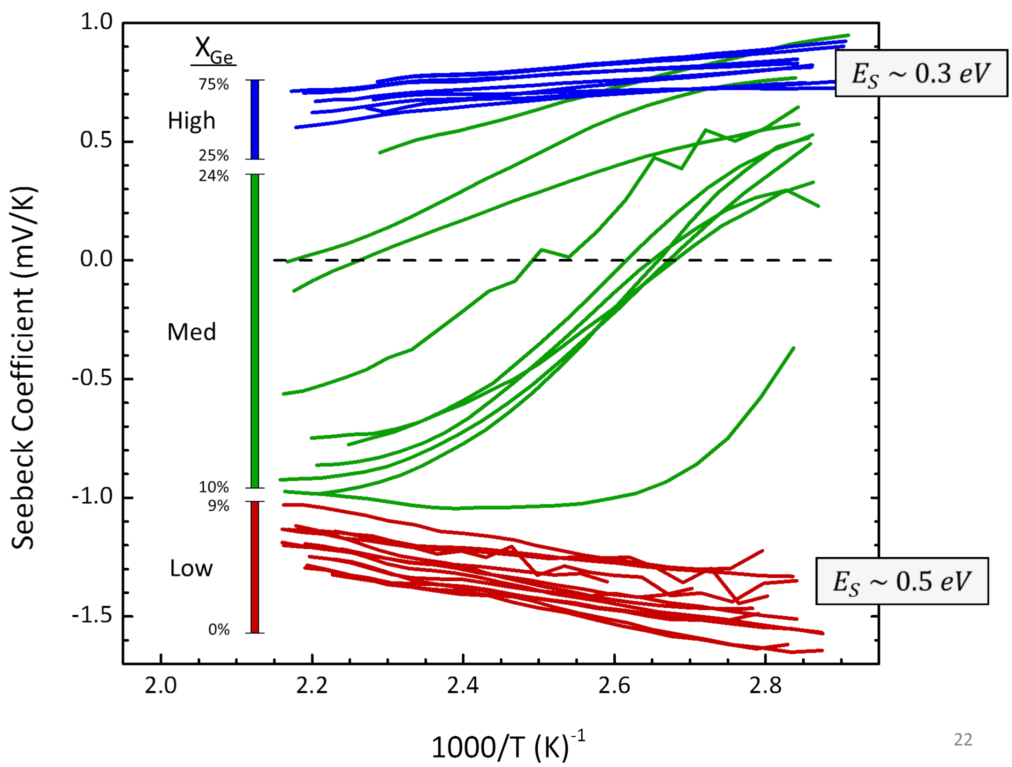
Similar to c-Ge
$X_{Ge}$
75%
High
25%
9%
Low
0%
$E_S \sim 0.3\ eV$
$E_S \sim 0.5\ eV$
Seebeck Coefficient (mV/K)
1.0
0.5
0.0
-0.5
-1.0
-1.5
2.0
2.2
2.4
2.6
2.8
$1000/T_{Avg}\ (K)^{-1}$


20

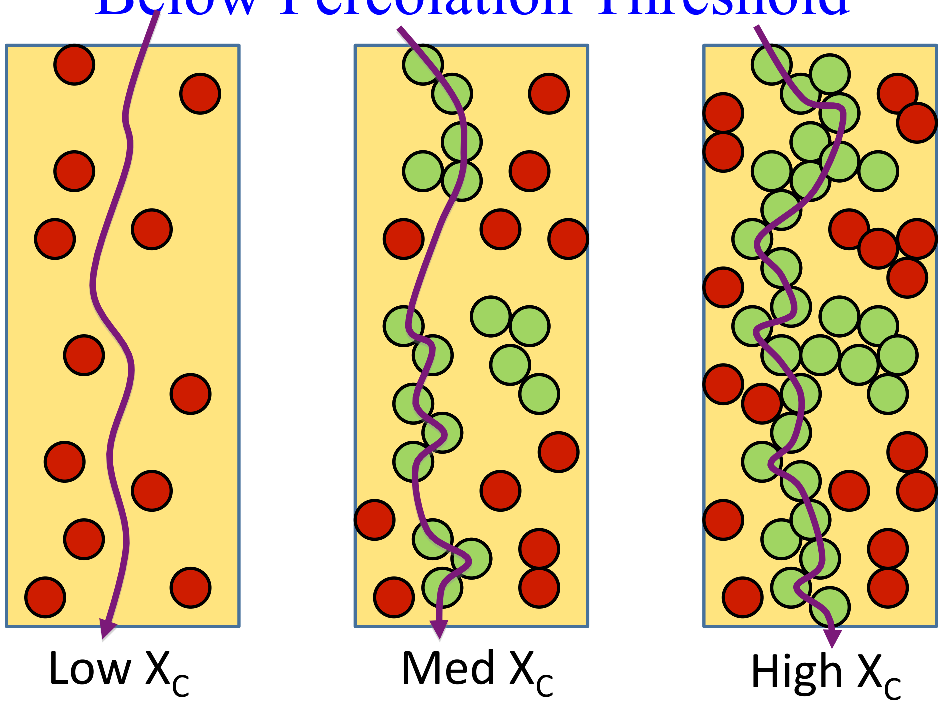





K. Bodurtha and JK, J. Appl. Phys. **114**, 193705 (2013)

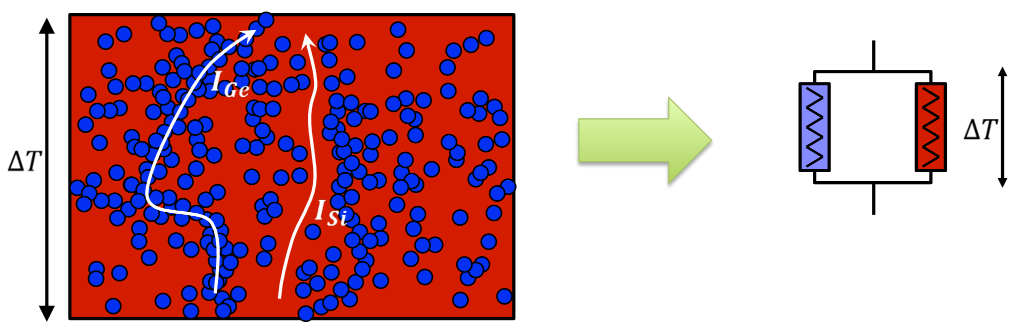


# Can See Influence of nc-Ge Chains Below Percolation Threshold



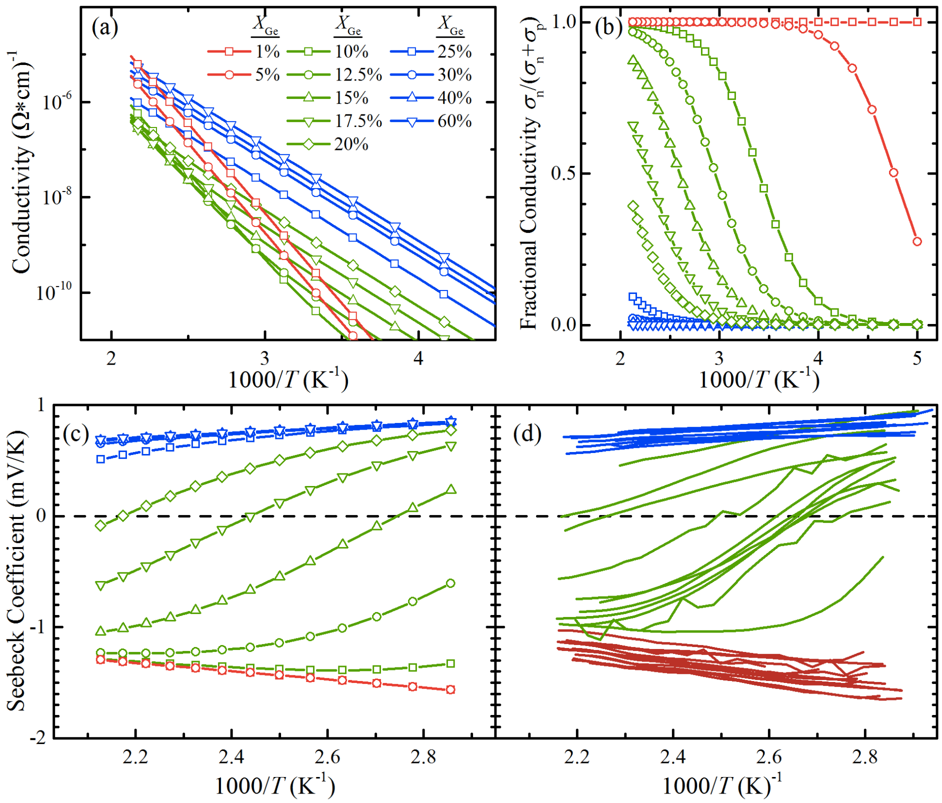


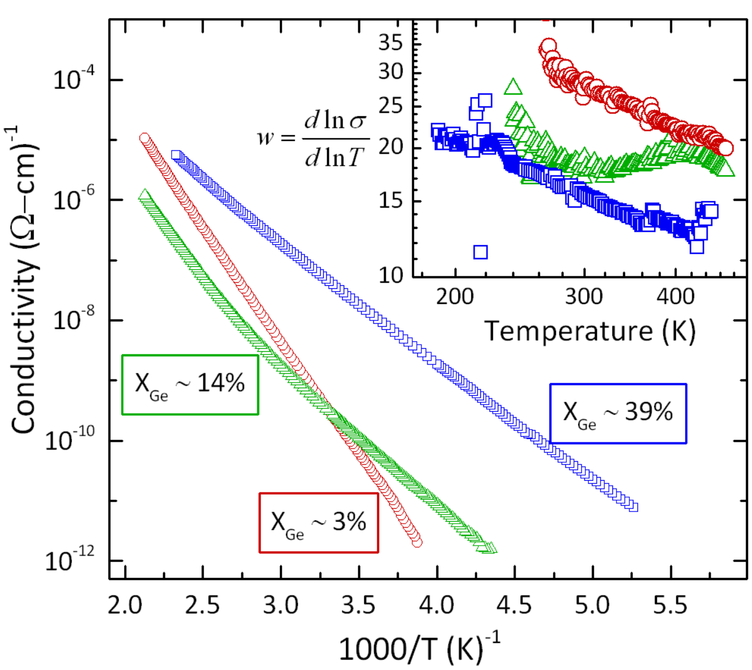

# Parallel Resistor Model



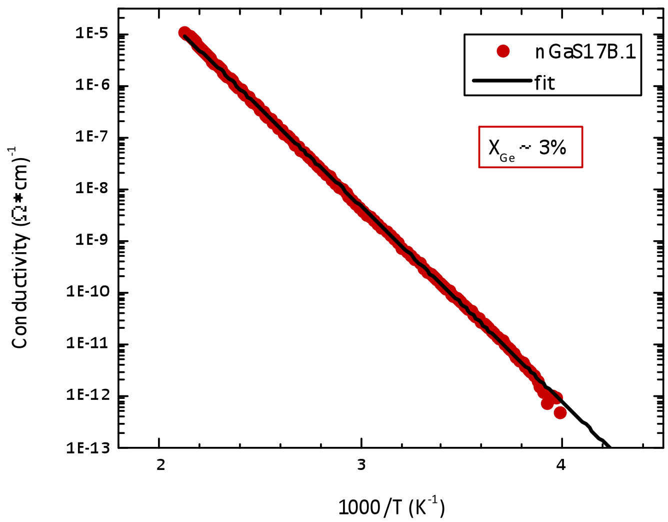

| | |
|---|---|
| Conductivity is weighted by the cross-sectional area of each resistor, which is proportional to $X_{Ge}$ | $\sigma(T) = \boxed{X_{Ge}\sigma_{Ge}} + \boxed{(1 - X_{Ge})\sigma_{Si}}$ |

| | |
|---|---|
| Thermopower is weighted by the conductivity: | $S(T) = \frac{\boxed{X_{Ge}\sigma_{Ge}}\, S_{Ge} + \boxed{(1 - X_{Ge})\sigma_{Si}}\, S_{Si}}{\sigma(T)}$ |


(a)
(b)
(c)
(d)
Conductivity (Ω*cm)^-1
Fractional Conductivity σn/(σn+σp)
Seebeck Coefficient (mV/K)
1000/T (K^-1)
1000/T (K)^-1
XGe
1%
5%
10%
12.5%
15%
17.5%
20%
25%
30%
40%
60%


Conductivity (Ω−cm)^-1
1000/T (K)^-1
w = d ln σ / d ln T
Temperature (K)
XGe ~ 14%
XGe ~ 39%
XGe ~ 3%

# Is Conductivity of nc-Ge/a-Si:H Arrhenius?

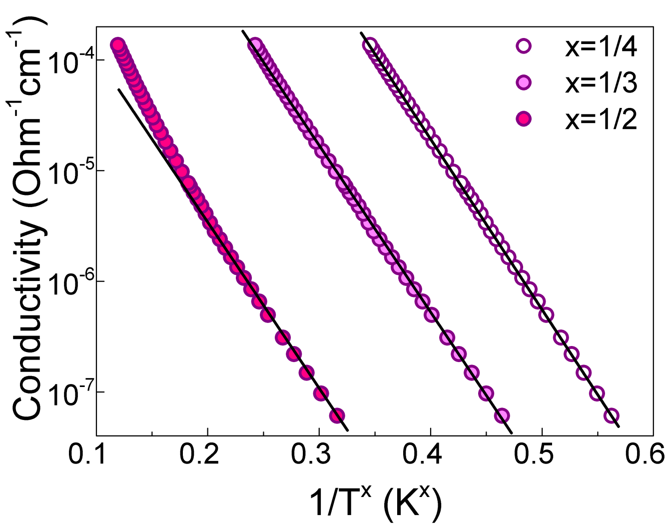





# How to Determine Temperature Dependence of Conductivity?

Change plot format to yield straight line

Often ambiguous - Temperature range too small



# How to Determine Temperature Dependence of Conductivity?

## Reduced Activation Energy Analysis

**Zabrodskii and Shlimak**, *Sov. Phys. Semicond.* (1975); **Hill**, *Phys. Stat. Solidi* (1976).

$$\sigma = \sigma_o \exp[-(T_o / T)^x]$$

Calculate w(T) from σ (T) data

$$w(T) = \frac{d\ln(\sigma)}{d\ln(T)} \quad \longrightarrow \quad w(T) = x\left(\frac{T_0}{T}\right)^x$$

# Reduced Activation Energy Reflects Conduction Mechanism

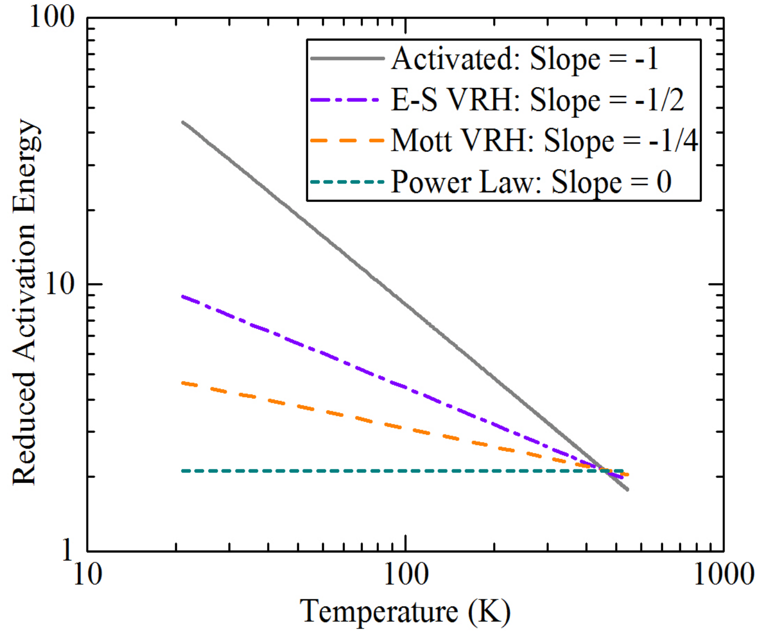
$$\sigma = \sigma_o \exp[-(T_o / T)^x] \quad \longrightarrow \quad w(T) = x\left(\frac{T_0}{T}\right)^x$$

| | | |
|---|---|---|
| Simple Activated Behavior | $x = 1$ | *log* W(T) ~ (-1) *log* T |
| Mott – Variable Range Hopping | $x = 1/4$ | *log* w(T) ~ (-1/4)*log* T |
| Efros-Shklovskii VRH | $x = 1/2$ | *log* w(T) ~ (-1/2)*log* T |
| Power Law Temp Dep. | $\sigma \sim T^n$ | d*log* σ/d*log* T = W = n |

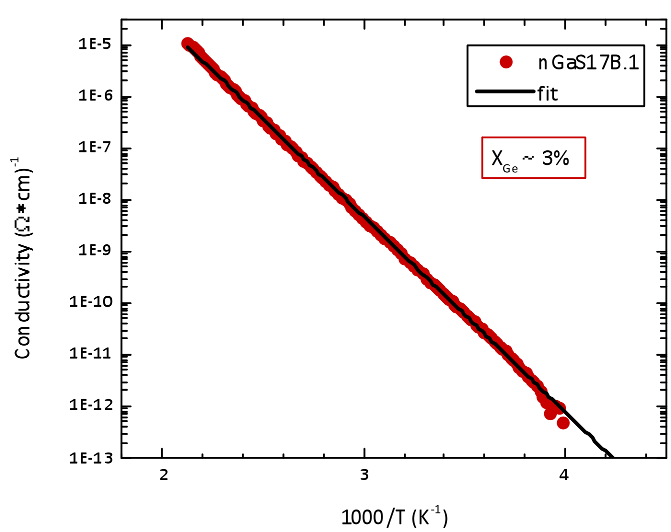
**Zabrodskii and Shlimak**, *Sov. Phys. Semicond.* (1975); **Hill**, *Phys. Stat. Solidi* (1976).

# Log-Log Plot of Reduced Activation Energy against Temperature Indicates Power-Law Exponent

$w(T) = d\,ln(\sigma)/d\,ln(T)$

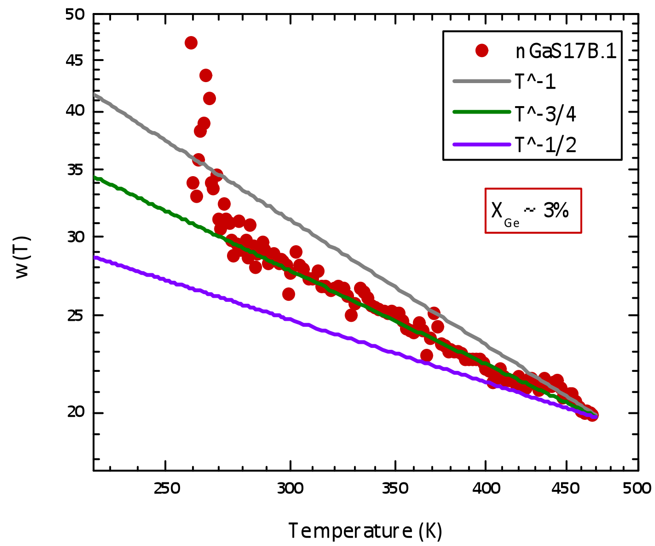



# Apply the Zabrodskii Analysis Technique to nc-Ge/a-Si:H



# Zabrodskii Analysis Finds Best Fit for $\kappa \sim 3/4$

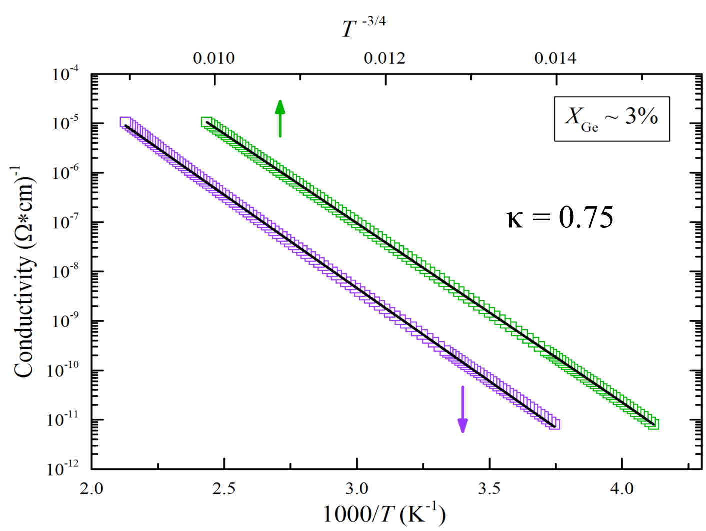
$$w(T) = d\,ln(\sigma)/d\,ln(T)$$




K. Bodurtha and JK, J. Appl. Phys. **118**, 215103 (2015)

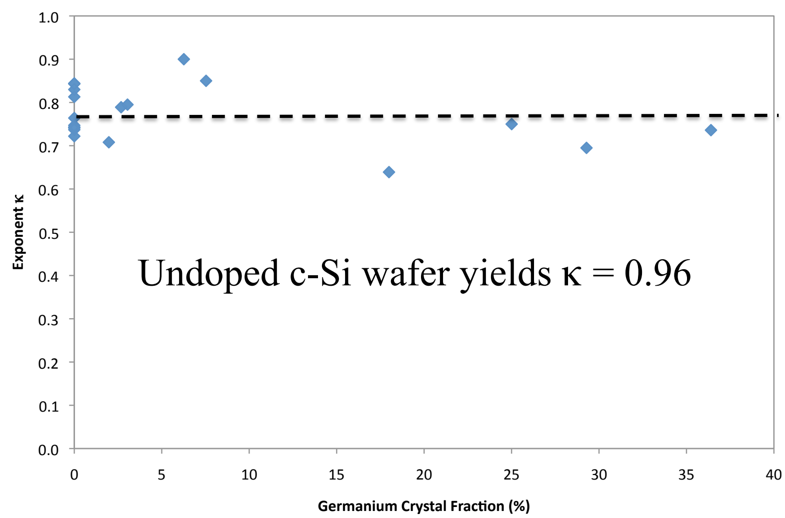


# $\sigma = \sigma_o \exp[-(T_o/T)^{\kappa}]$

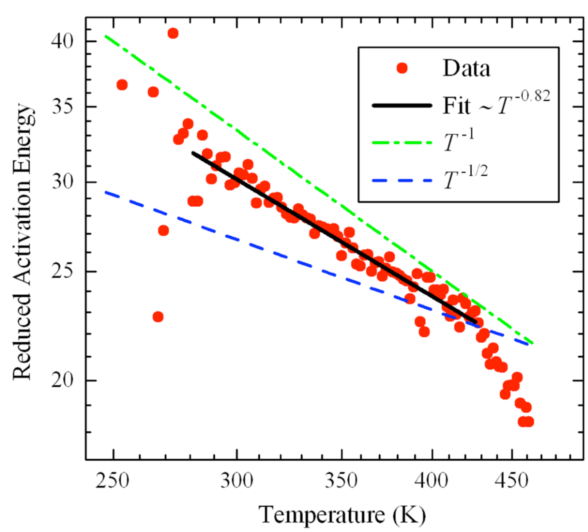


# Power-Law Exponent κ vs. nc-Ge Content

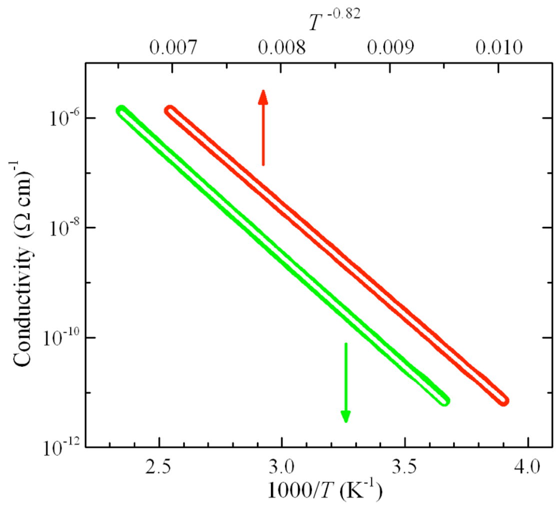
$$\sigma = \sigma_o \exp[-(T_o/T)^{\kappa}]$$
$$0.7 < \kappa < 0.84$$



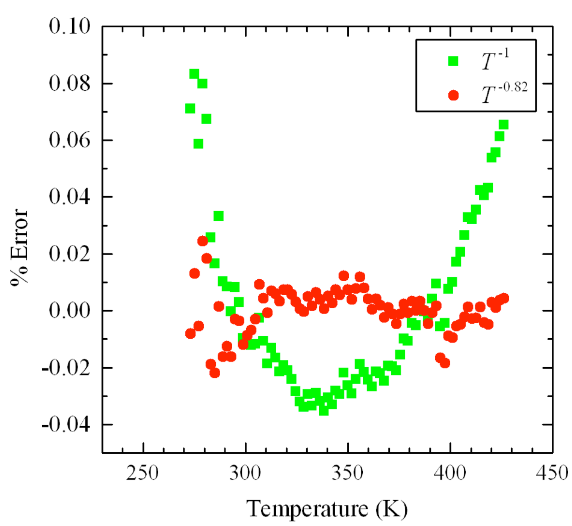

# Reduced Activation Energy Plot for a-Si:H



# Arrhenius vs. Anomalous Hopping Temperature Dependence




# Difference between Data and Arrhenius and Anomalous Hopping Expression



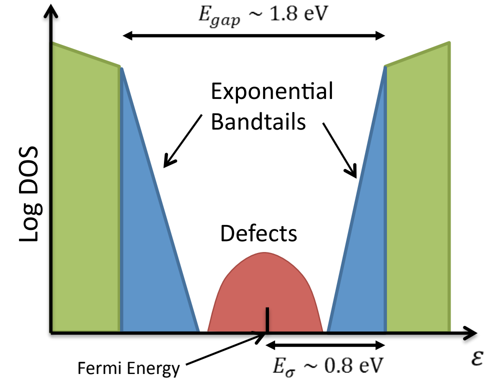
# Hopping in Exponential Band Tail States

Current is carried by free electrons thermally excited into the conduction band.

Bandtails don't contribute to conduction because DOS is too small and states are too far apart for wavefunctions to overlap.

$$\sigma(T) = \sigma_0 \exp\left[-\frac{E_\sigma}{k_B T}\right]$$

*N. F. Mott, Advances in Physics **16**, 49 (1967).*

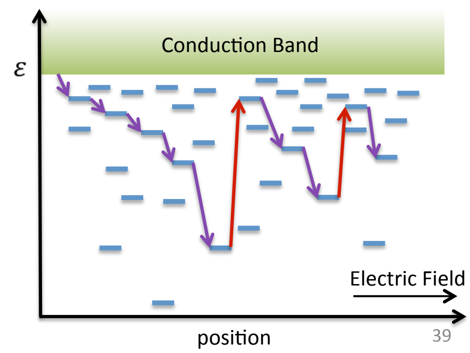



If bandtails are sufficiently broad, and/or $T$ is small, hopping through bandtail states can become significant

Hop to nearby states, always hopping down in $\varepsilon$

Occasionally thermally promoted back up to higher energies.

*Grunewald and Thomas (1979); D. Monroe, (1985).*






# Hopping Through Bandtail States

Simulations based upon model of hopping through exponential bandtails

Assume conduction occurs through band of states at transport energy of width $W = (6\varepsilon_o\, kT)^{1/2}$

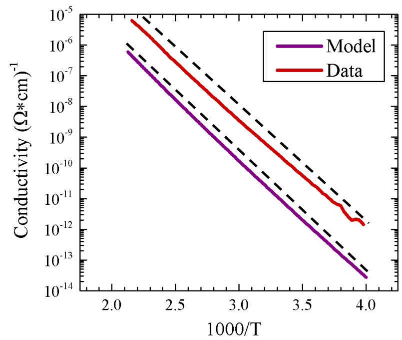
*Shklovskii, Levin, Fritzsche and Baranovskii (1990)*

# Hopping Through Bandtail States

Simulations based upon model of hopping through exponential bandtails

Assume conduction occurs through band of states at transport energy of width
$W = (6\varepsilon_o\, kT)^{1/2}$

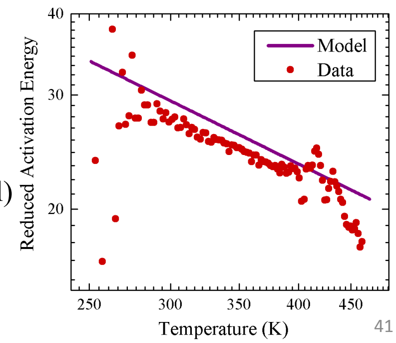
*Shklovskii, Levin, Fritzsche and Baranovskii (1990)*




For $\varepsilon_o = 50$ meV
$N = 10^{20}$ cm$^{-3}$
a = 1.5 nm (dist between adjacent states)
$\varepsilon_F = 0.85$ eV
$\nu_o = 10^{15}$ sec$^{-1}$

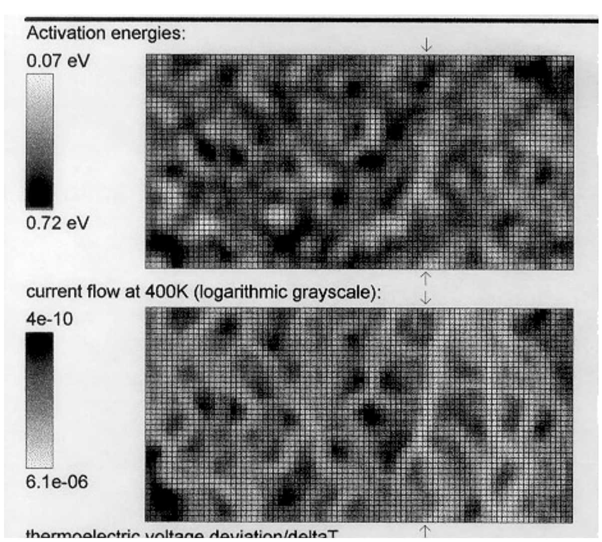
κ= 0.78 (model)

κ= 0.76 (data)






# Simulations Show Current Filaments Arise from Spatial Variations of Resistance

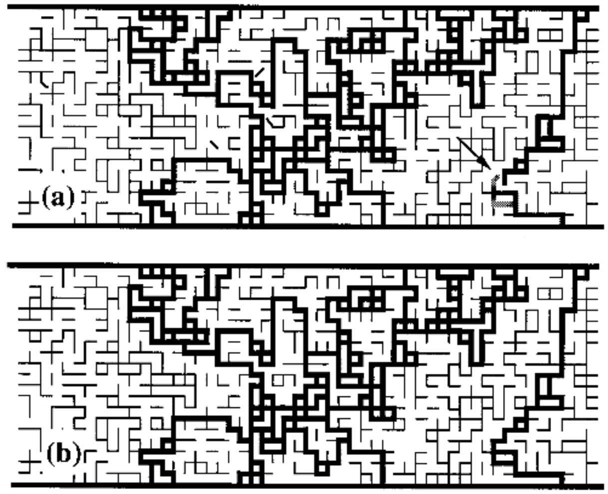



X-Y Grid of Resistors

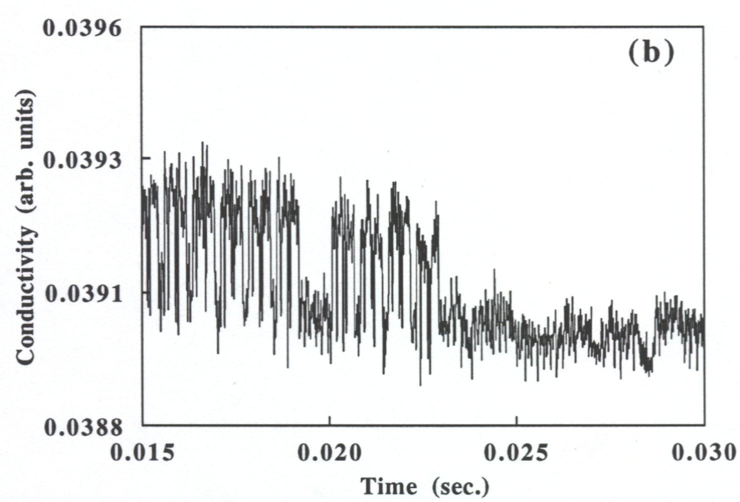
$R = R_o \exp[E_a/kT]$

D. Quicker and JK,
Phys Rev B **60** (1999)

# Dynamical Percolation Model Simulates Effect of H Motion on Inhomogeneous Current Filaments

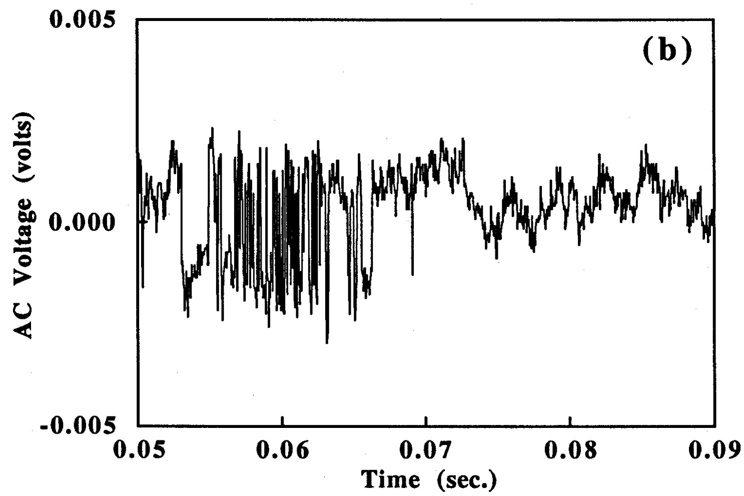



# Simulated Current Fluctuations Show Both RTSN and 1/*f* Noise

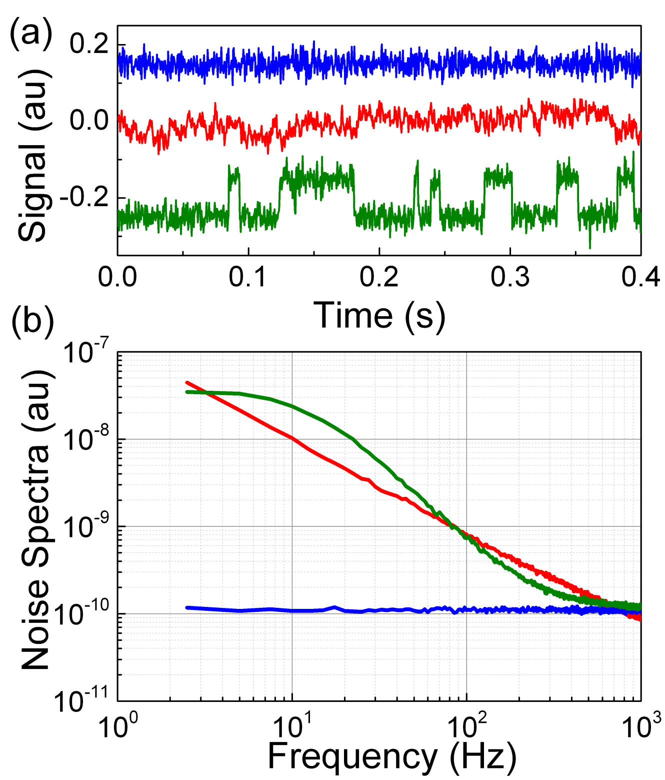



L. Lust and JK, Phys Rev E (1994); Phys Rev Lett **75** (1995)

# Consistent with Measured Current Fluctuations




L. Lust and JK, Phys Rev E (1994); Phys Rev Lett **75** (1995)

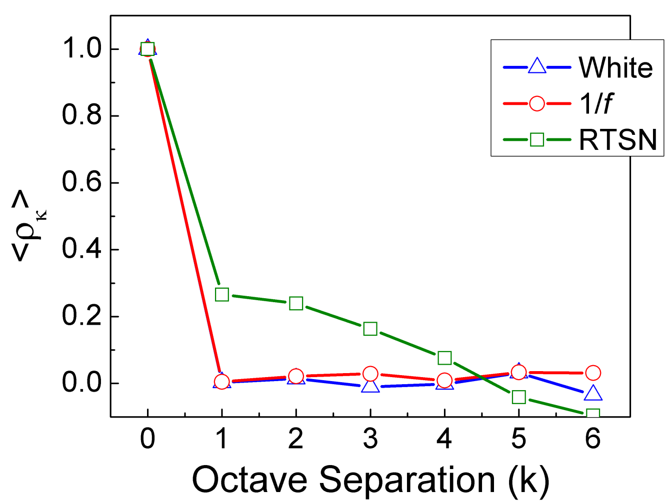


# Correlation Coefficients Quantify Interactions Across Frequency Octaves

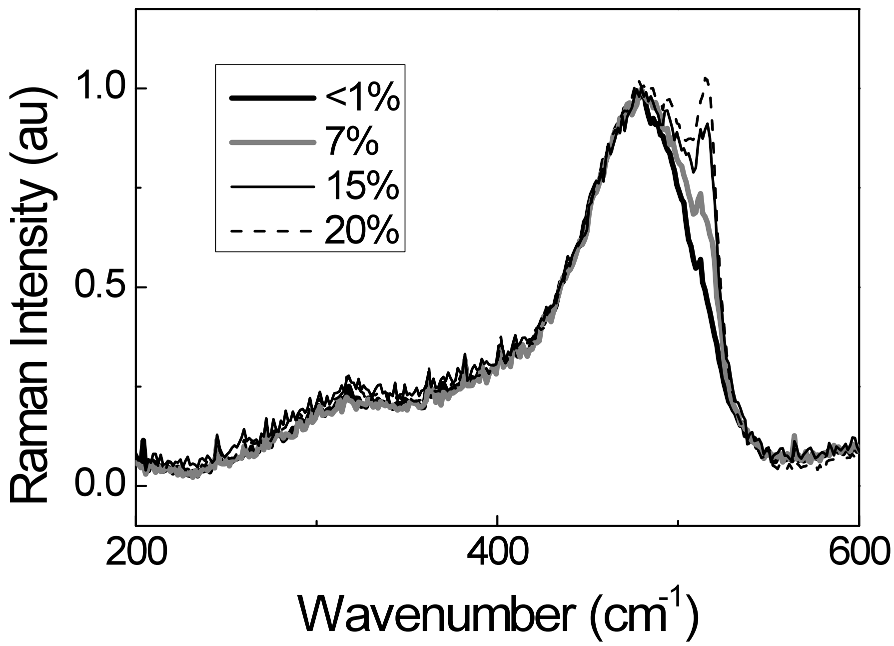
$$\rho_{ij} = \Sigma \frac{(NP_i - \langle NP_i \rangle)(NP_j - \langle NP_j \rangle)}{(K - 1) \quad \sigma_i \; \sigma_j}$$

$NP_i$ = Noise Power in Octave i (i = 1 - 7)
$\langle NP_i \rangle$ = Average Noise Power in Octave i
$\sigma_i$ = Standard Deviation of Average Noise Power in Octave i
K = 1 – 1024 FFT's

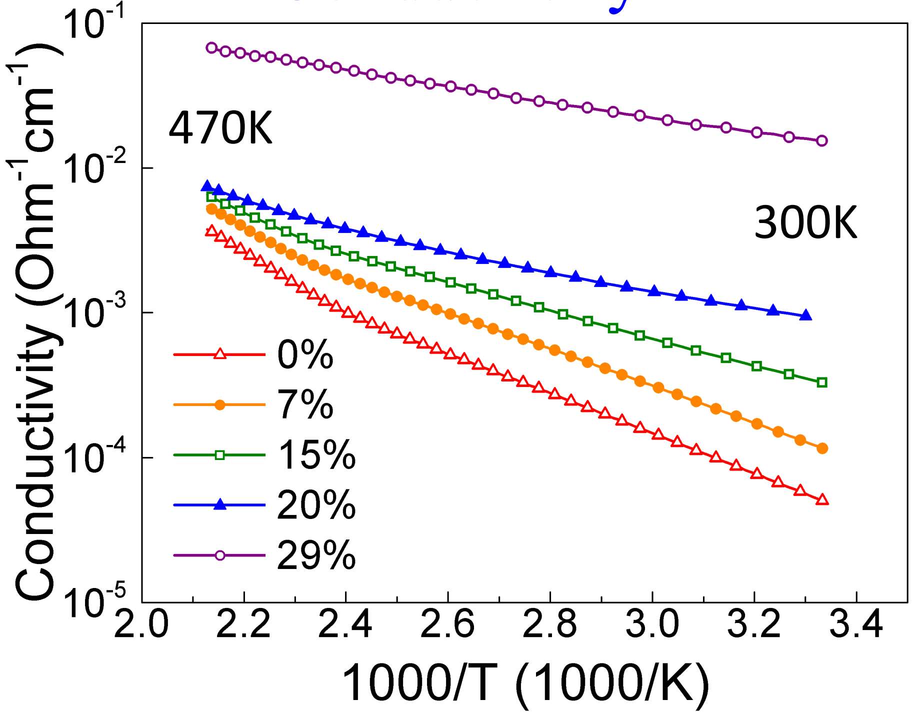
# Simulated Correlation Coefficients

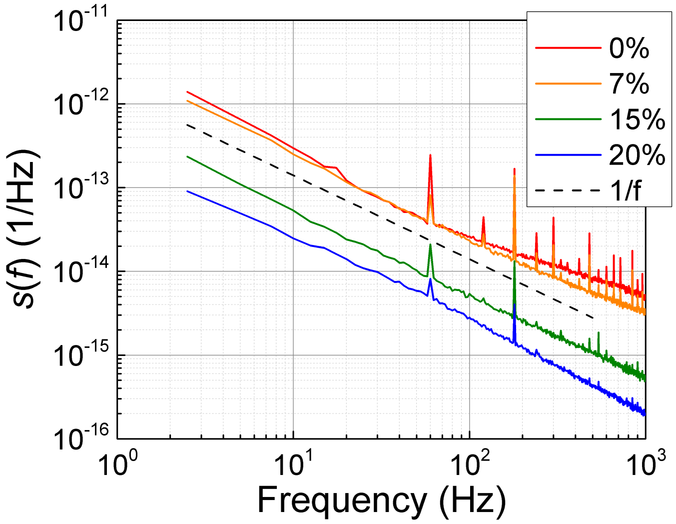


# N-Type Doped a/nc-Si:H Films – Raman Spectra

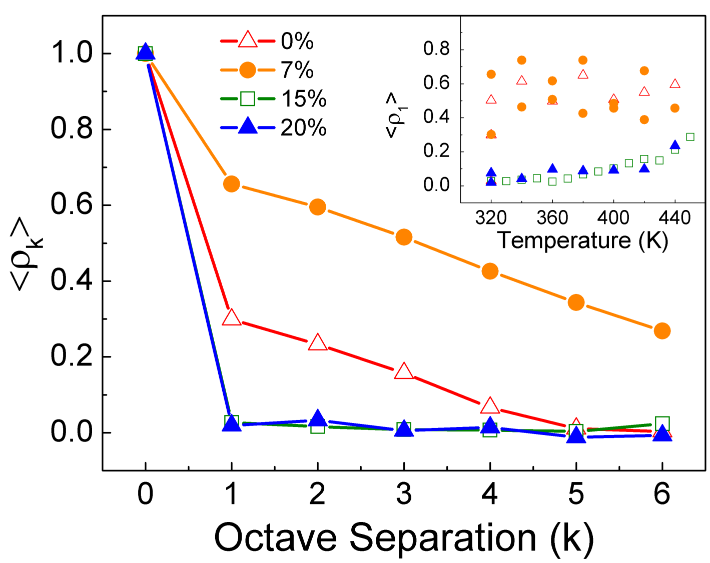



# Conductivity



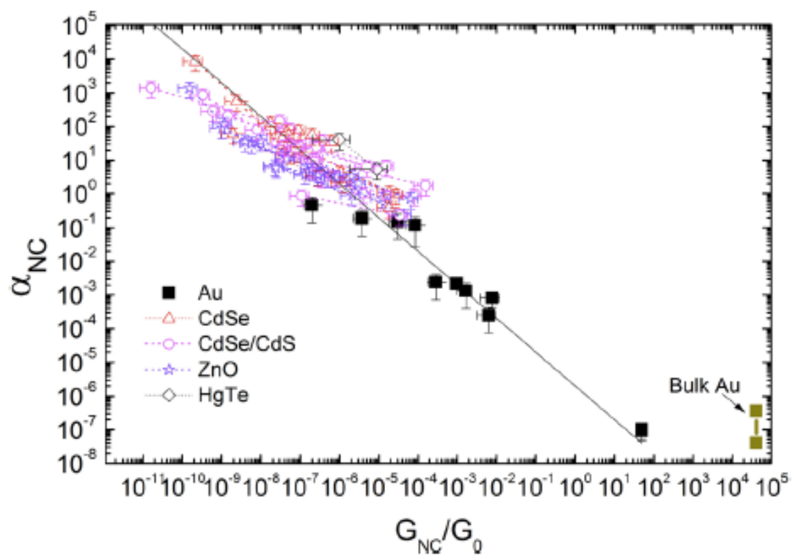


$10^{-11}$
$10^{-12}$
$10^{-13}$
$10^{-14}$
$10^{-15}$
$10^{-16}$
$s(f)$ (1/Hz)
$10^{0}$
$10^{1}$
$10^{2}$
$10^{3}$
Frequency (Hz)
0%
7%
15%
20%
1/f

1.0
0.8
0.6
0.4
0.2
0.0
$<\rho_k>$
0
1
2
3
4
5
6
Octave Separation (k)
0%
7%
15%
20%
0.8
0.6
0.4
0.2
0.0
$<\rho_1>$
320
360
400
440
Temperature (K)

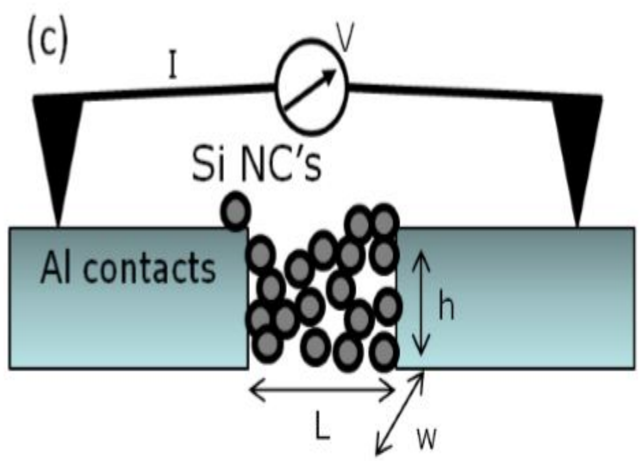
# 1/*f* Noise in QD Very Sensitive to Nearest Neighbor Conductance



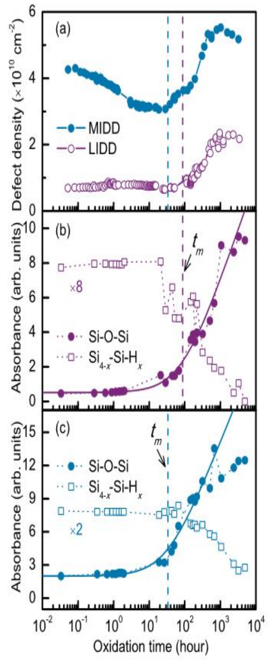

H. Liu, E. Lhuillier, and P. Guyot-Sionnest, J. Appl. Phys. **115**, 154309 (2014)

# Free-Standing Nanocrystal Films

- Substrate with Pre-Deposited Electrodes Underneath Injection Tube from Nanocrystal PECVD
- Si Nanocrystals deposited on top of electrodes

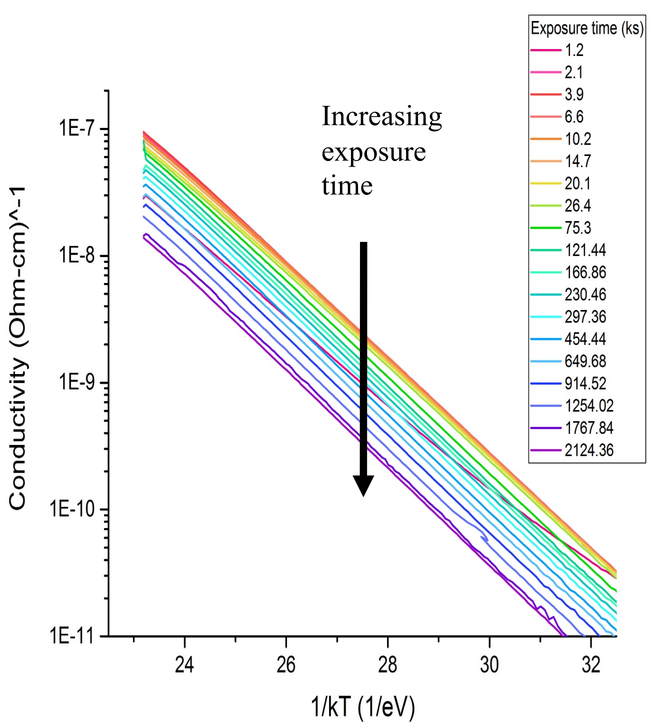


# Oxides Grow Slowly on Si nc

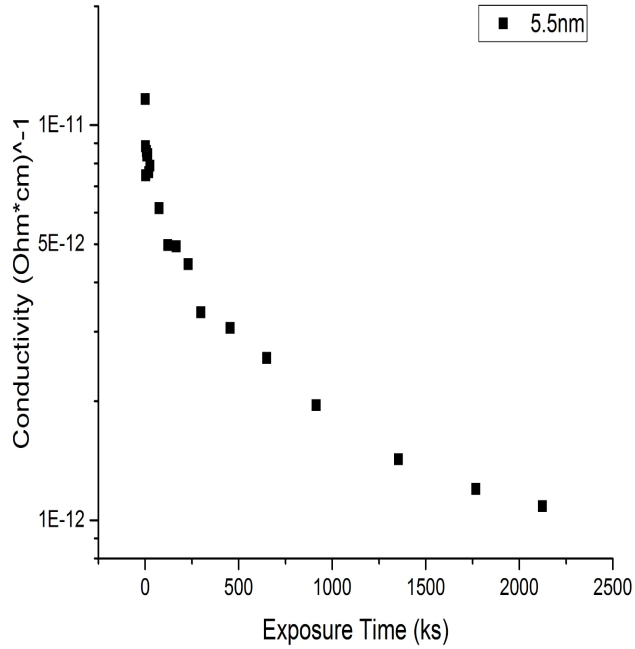



R.N. Pereira, D. J. Rowe, R. J. Anthony, and U. Kortshagen. Phys. Rev. *B* **86** 085449(2012).

# Dark Conductivity Decreases With Atmosphere Exposure

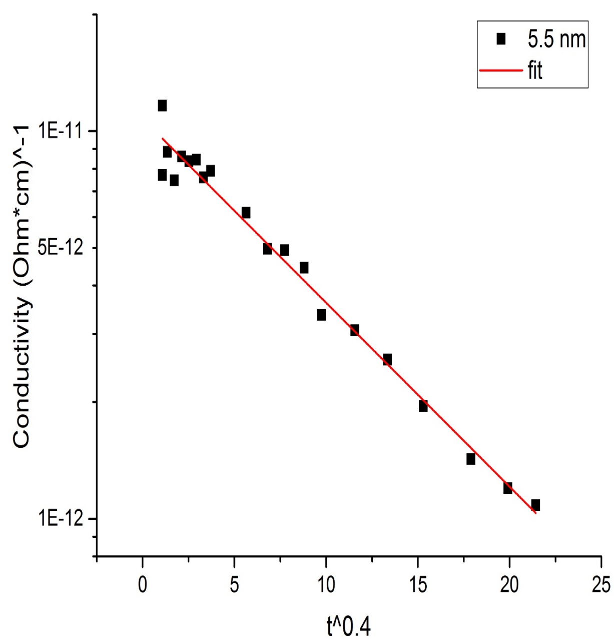


# Conductivity Decreases with Increasing Air Exposure

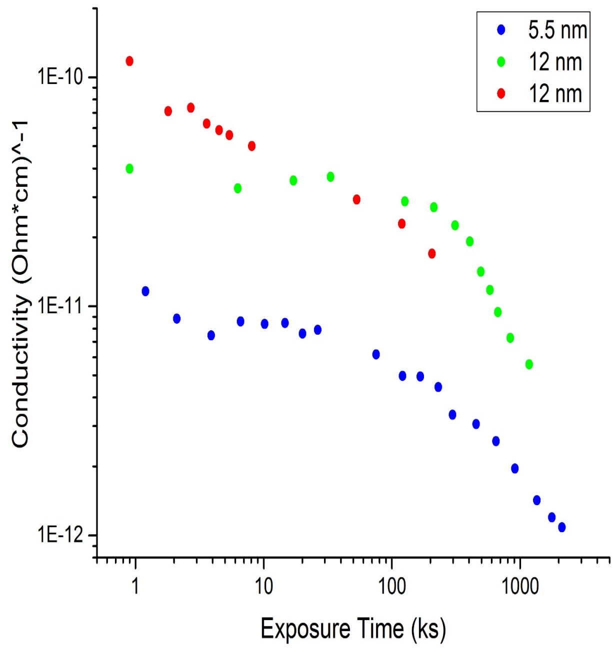



# Conductivity Follows Stretched Exponential Dependence on Air Exposure Time

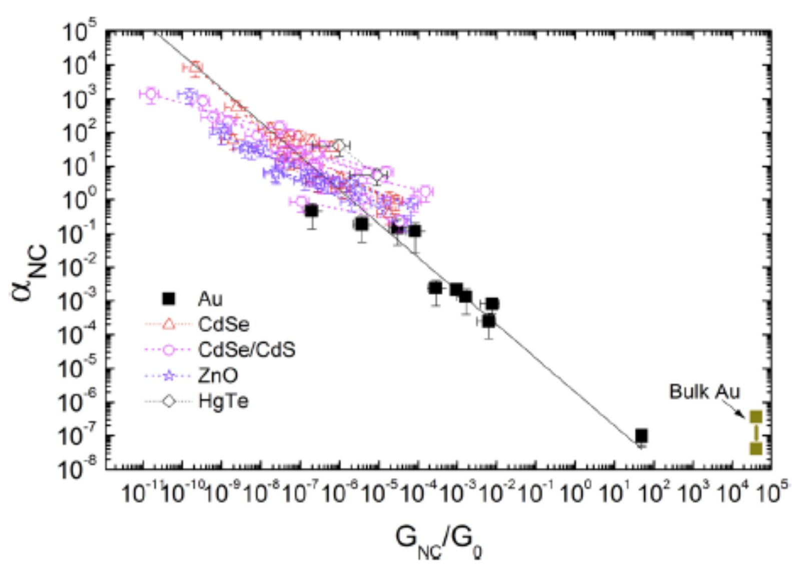
- Stretched exponential: $\sigma = \sigma_0 e^{-(t/\tau)^{\beta}}$
- Here $\beta = 0.4$
- $\tau = 255\ ks$



# Decrease of Conductivity with Atmosphere Exposure Sensitive to nc Size




# 1/*f* Noise in QD Very Sensitive to Nearest Neighbor Conductance

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# Summary

- Conduction In Amorphous/Nanocrystalline Composites Can Display Behavior Not Seen in Either Material Separately

- Anomalous Hopping ($\kappa \sim 3/4$) Observed in nc-Ge/a-Si:H and a-Si:H

- Transport in Free-Standing Si nc Films is Sensitive to Air Exposure